

Controlled-Potential Coulometry

Controlled-potential coulometry (CPC) is used for quantitative analyses when high accuracy and precision (0.1 to 0.5%) are required and sample size is limited. We typically use CPC for major constituent assays of solutions, alloys, nonmetallic materials, and compounds. This technique is also used as a standardization or umpire technique for other quantitative methods, for oxidation state analyses, and studies of electrochemical reactions.

Principle of Technique

The substance to be determined is electrolyzed completely in a portion of the sample solution in a special electrolysis cell. The electrolysis current required is integrated and used as a measure of the quantity of the substance electrolyzed. Working electrode potential is controlled to give selectivity. Analytical results are usually based on the electrical calibration of the integrator rather than on chemical standards.

Samples

Form. Samples must be dissolved in a solution suitable for electrolysis, usually an aqueous acid solution.

Size. Samples must provide 1 to 10 mg of analyte for each determination.

Preparation. Solutions can often be analyzed as received or after dilution. Solids must be dissolved, usually in acids.

Limitations

CPC is applicable primarily to elements in the middle of the periodic table, including the actinides, organic nitro compounds, halides, and other compounds that are oxidizable or reducible in aqueous solution.

Organic constituents must be completely destroyed before an inorganic constituent analysis can be performed.

This method is not recommended for trace or minor impurity analyses. Qualitative knowledge of sample composition is required.

Estimated Analysis Time

After solution preparation, 5 min to 1 h per determination is required.

Capabilities of Related Techniques

Titrimetry and gravimetry have comparable accuracy and precision. They are generally applicable to the same types of samples as CPC but require larger amounts of analyte and may be more or less selective.

Controlled-potential electrolysis can be used for chemical synthesis and to separate constituents before other measurement techniques are applied.

Voltammetry and polarography measure the electrolysis current potential characteristics of solutions. These methods may be more suitable for minor constituent and trace analyses than CPC.

Examples of Applications

- Assay of precious-metal materials and plating solutions that contain gold, silver, palladium, or iridium.
- Measurement of total uranium and oxidation states in uranium oxide.
- Assays of organic compounds that contain nitro groups (i.e., explosives).
- Determination of molybdenum in molybdenum-tungsten alloys.
- Measurement of Fe(III)/Fe(II) ratios in nuclear waste forms.

